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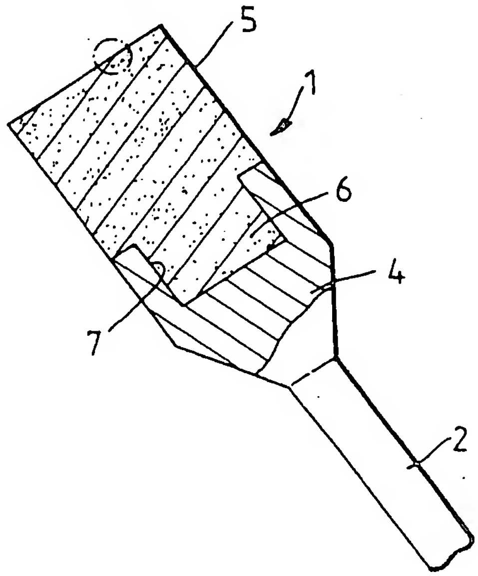
(54) **Method for the production of a chemically bounded ceramic product, a tool to be used for the carrying out of the method, and an interchangeable part on the tool.**

(57) The invention relates to a method for manufacturing a chemically bounded ceramic by reaction between one or several pulverulent binding agents and a liquid which reacts with these binding agents, wherein the ceramic product also can include one or several aggregates, which essentially do not take part in the chemical reactions. An amount of pulverulent material consisting of said binding agent and possible aggregate material is blunged in said liquid so that all powder grains are caused to effectively contact the liquid. The obtained slurry or slip is drained so that the main part of surplus reacting liquid is removed. An amount of the mixture of powder and reacting liquid which still exist to some extent in the mixture is applied in a mould cavity, and additional liquid is removed in situ in the mould cavity before the product is caused to harden through reaction between said binding agent and remaining liquid. The invention also relates to a tool for the carrying out of the method, comprising a preferably exchangeable working part (5) consisting of a solid porous material.

Fig. 2.



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TECHNICAL FIELD

The present invention relates to the field of Chemically Bounded Ceramics (CBC) for the manufacturing of which chemical reactions, e.g. hydration processes, are used for the bounding operation at temperatures - normally below 100°C - which are so low that conventional sintering can not be applied. Mer particularly the invention relates to a method for the manufacturing of a chemically bounded ceramic by reaction between one or several pulverulent binding agents and a liquid which reacts with these binding agents, wherein the ceramic product also can include one or several aggregates, which essentially do not take part in the chemical reactions. The method of the invention is developed in the first place for the manufacturing of permanent tooth filling materials, but is generally useful for the manufacturing of a ceramic in a cavity, e.g. in conncection with repairing prostethis, machine elements, household utensils, and ornaments indoors and outdoors, particularly for repairing statues and ornaments damaged because of environmental pollution.

BACKGROUND ART

Materials intended for permanent tooth fillings must satisfy a number of demands. Some of these demands may be difficult to satisfy at the same time. The same combination of requirements often are valid also for implant materials. Among these requirements for example the following can be mentioned.

- The material shall have adequate mechanical features, in the first place a good strength and, as far as dental materials are concerned, also a good wear resistance.
- It shall be biological compatible, a feature which is particularly important for implant materials.
- It shall have an adequate corrosion resistance.
- The material shall have a good long term stability, which implies that it must neither shrink nor expand because of ageing, a feature which is of extreme importance for tooth filling materials.
- The starting material shall have a good workability and provide a fast but not too fast initial hardening.
- The material must not be toxic or generate toxic secondary products.

An example of a material which can be defined as a CBC-material is that "cement" which is used in the field of dentistry and which is based mainly on zink oxide and orthophosphoric acid. This cement has been used for temporary fillings, fastening of crowns, etc., but its strength has so far been unsatisfactory and this cement can therefor not be used for permanent fillings.

Another type of material used for dental applications are the so called glass polyalkeonate cements and similar materials. The Swedish Patent 381 808 and the European Patent Publications No. 0 024 056 and 0 115 058 exemplify this type of material.

It has also been suggested to use hydraulic cement materials as dental fillings. Thus, the US Patent No. 4 689 080 describes the use of calcium aluminate as a binding agent for dental applications. Also a material which is described in the International Patent Application No. WO90/11066 is based on the use of one or several pulverulent binding agents, and a liquid which reacts with these binding agents, which may consist of calcium aluminate or other hydrations phases, such as silicates and phosphates, while said liquid consists of water. In order to achieve a sufficient strength, a powder body is formed consisting of the said binding agent and possible aggregate, wherein the powder body without addition of the said liquid is compacted by subjecting the powder body to an external pressure prior to soaking (impregnating) the green body with said liquid, the external pressure being so high and the temperature being so low that there is achieved a well united green body without any sintering reactions occurring during the compacting, in which green body the filling density is increased to at least 1.3 times the initial filling density. The compaction is carried out through mechanical pressing, preferably cold isostatic pressing. This green body thereafter is impregnated with the liquid which is soaked in by capillary forces acting in the body. The spontaneous soaking in by means of the capillary forces also can be augmented by shaking or vibrating the green body or subjecting it to a similar treatment in the liquid. Through the soaking, the filling density of the green body is increased to at least 1.5 and preferably to at least 1.8 times the initial filling density. By this technique it has been possible to achieve a material which potentially can satisfy all the above mentioned features. However, clinical tests have shown that in some cases one of the requirements has not been satisfied, namely the demand for long term stability. Thus after an extended period of time there has been registered an expansion in the ceramic. It is true that the expansion degree is very small but for tooth fillings it is nevertheless hazardous since it may cause fatal tooth fractures. Probably not the entire pore system in the green body is filled with liquid in connection with the soaking of the green body, in spite of all stimulating measurements, which is believed to cause the expansion. The incomplete filling of the pore system in turn may be due to an initial reaction between liquid and binding agent in surface layers or in deeper parts of the material which may prevent continued diffusion of liquid to regions of the powder body which have been isolated because of the said reactions. This has to the result that in these isolated regions of the product

there may exist non-hydrated calcium aluminates, when the product is based on that type of binding agent. If water or corresponding liquid later will diffuse into the non-reacted regions, which may occur after several years, a continued hydrating or corresponding reaction will take place, which will cause an expansion of the material and in fatal cases crack the product.

BRIEF DISCLOSURE OF THE INVENTION

It is an object of the invention to provide an improved chemically bounded ceram. As starting material may be used the same raw materials as according to said WO90/11066, wherefore also the same chemical reactions which take place in the product in connection with the stiffening will be the same. The difference lies in the practical performance which aims at eliminating all risk that all parts of the product are not completely wetted. Thus, according to the improved method of the invention, there is not made any green body of dry powder in order to achieve a high initial dense packing degree. Instead the said binding agent and possible aggregate materials are blunged in the said liquid, so that all grains of the powder are effectively brought to contact (be wetted by) the liquid prior to initial compaction. The slurry or slip thereafter is drained so that the main part of surplus reacting liquid is removed, whereafter an amount of the mixture is applied in a mould cavity, i.e. in a tooth cavity. The mixture which is applied in the cavity consists of powder and reacting liquid which still exist to some excess in the mixture, i.e. to an extent larger than is required for the transformation of all pulverulent binding agent through chemical reaction. Thereafter additional liquid is removed <u>in situ</u> in the mould cavity before the product is hardened through reaction between the said binding agent and the remaining liquid. More particularly, the said additional liquid is preferably removed <u>in situ</u> by means of a tool - a compaction tool - with a part acting on the moist pulverulent material, said part consisting of a hard, porous material, into which said additional liquid is sucked in at the same time as the pulverulent material is compacted in the mould cavity to reach a compaction degree exceeding 60 volume-% solid phase, preferably more than 62 %. Suitably there is used a compaction tool, which per se is part of this invention, where the pores in the said porous material has a mean pore size which is smaller than the mean grain size of the powder mixture to prevent the powder grains in the powder mixture to enter into the pores in the tool.

Suitably the tip portion of the tool, which is brought into contact with the powder-liquid mixture, consists of an exchangeable member of the tool. This member can consist of a porous ceramic material, by a porous metallic material, or by a porous polymeric material. Also combinations of these materials are per se conceivable.

The compaction tool can have the same shape as a conventional so called stopper of the kind which is used by dentists, when it is the matter of making tooth fillings, wherein the stopper head or tip portion consists of or comprises or exhibits a porous stamp which sucks up excess liquid from the predrained powder/liquid mass which successively is filled into the tooth cavity or other cavity at the same time as the material is pressed together to the desired compaction degree. The risk for making the mass deplete of liquid is minimal since it is always the smallest pores/channels which are emptied last in connection with capillary action. If, however, there would nevertheless be a deficiency of liquid, it is easy to adjust the moisture content by remoistening and a repeated press suction. After completed compaction more reacting liquid, i.e. water or corresponding, may be supplied. The use of a porous stopper thus implies a combined suction and pressure action which is an efficient method of achieving an optimal compaction at the same time as the compacted mass is not depleted of reacting liquid.

Through the method of the invention there is achieved a compaction degree of at least 60 volume-%, preferably at least 62 volume-%, suitably 62-67 volume-% prior to reaction between liquid and binding agent and in the finished reacted product a very low degree of porosity, which means less than 5 volume-% and preferably less than 2 volume-% porosity as measured by penetration of water according to Archimedes' principle.

Further there is achieved a complete or almost complete transformation of the binding agent or the binding agents, i.e. a complete reaction between the binding agent or binding agents and the reacting liquid, which is an unconditional demand.

According to a first preferred embodiment of the invention, said binding agent consists of one or several hydraulic binding agents, the hydration phases of which belong to the group of compounds, which consists of aluminates, silicates, and phosphates, the liquid being a hydration liquid, consisting of water and possibly substances dissolved in the water. The preferred aluminate is calcium aluminate, which can be present in various proportions between CaO and Al_2O_3. The preferred silicate is calcium silicate with varying proportions between CaO and SiO_2, which is the main component of Portland cement, which however contains also other components, e.g. Al_2O_3. Other phases are e.g. 3 $CaOxAl_2O_3$ and 4 $CaOxAl_2O_3$ and 4 $CaOxAl_2O_3xFe_2O_3$.

Combinations of silicates and aluminates having a higher portion of aluminate than in an ordinary Portland cement are also useful. Phosphates, which are useful as binding agents in this connection, are e.g. calcium

phosphate and zinc phosphate.

The above mentioned substances may exist as natural minerals or be produced synthetically. Irrespective of their origin they must be preliminarily treated according to conventional technique, which however does not constitute part of the present invention. As a result of this treatment a powder is obtained, in which the pulverulent grains have a size ranging from a submicron-size up to a maximum size of 100 μm in the largest extension of the grains. An ordinary medium grain size can be as high as about 15 μm, i.e. 50 percent by weight of the grains have a size larger than about 15 μm. Preferably the main part of the grains have a size between 10 and 30 μm. The shape is very irregular. It is true that the invention has been developed for hydration materials, e.g. aluminates, silicates, and phosphates, but the invention's principal features probably can be utilized also in other systems. In the dental field, and also in other fields, the invention can e.g. be utilized in case the binding agents mainly are one or several oxides, e.g. zinc oxide, while said liquid is one or several acids, e.g. a phosphorus-based acid, preferably and mainly orthophosphoric acid.

An additional feasible application field among several others is the production of a so called glass polyalkeonate cement, the binding agent possibly consisting of a mixture of a glass powder and a freeze-dehydrated acid according to a technique known per se, while the liquid can be water.

Besides the binding agent and the liquid, which subsequent to the reaction with the binding agent form a solid phase, it is possible, as is generally known, to add an aggregate material, i.e. a material which does not participate in the chemical reactions between the binding agent and the liquid but which is present as a solid phase in the finished, solid final product. For certain application fields such aggregate materials can be reinforcements of various types, e.g. fibers of metals, carbon, glass or organic materials etc. The reinforcement advantageously can be obtained by introducing long crystals, so called whiskers, e.g. of SiC, Si_3N_4 and/or Al_2O_3.

Also, for dental applications or as a prosthesis material for general surgical applications the CBC-material according to the invention can include aggregate materials, provided they meet certain requirements. Thus, they must not be toxic, they must be biocompatible, must not cause irritations in the oral cavity in the case of dental applications, must not corrode etc. A small amount of boron nitride can e.g. be added to be used as a solid lubricant in connection with the compaction of the dry pulverulent material, preferably an amount of 5-15 percent by volume of the dry substance previous to the compaction and the impregnation with said liquid.

In case the binding agent is one or several hydration materials, the aggregate material can also be e.g. hydroxylapatite or solid solutions thereof and/or oxides of one or several of titanium, zirconium, zinc and aluminum. It is particularly advantageous to use as aggregates outwardly projecting, needle-shaped crystals, preferably of titanium dioxide, which are biocompatible and chemically inert in all the systems considered here, i.e. also to such hydration liquids as phosphoric acid etc. Said titanium dioxide aggregate suitably comprises three-dimensionally oriented and star-shaped, needle-shaped crystals, the thickness of which can be a few tenths of a micrometer but the length of which normally is several times larger. These crystals are agglomerated to larger particles or agglomerates having a size of several micrometers. The reinforcement effect of the agglomerates in the hardened product is due to the nature of the agglomerates. Thus, the bond between the setting phase and the agglomerates of titanium dioxide crystals is improved and strengthened when the agglomerates are etched, e.g. in 0.5-10 M, particularly 1-3 M, sodium hydroxide or in another etch solution, e.g. a mineral acid such as phosphoric acid.

According to the invention a superplasticizer can also be admixed in a dry condition or by means of a water-free solution in the sludge or slip before this is dewatered. A suitable superplasticizer is e.g. 79 % hydrolysed polyvinyl acetate.

The aggregate particles or the agglomerates of aggregate particles preferably have a particle size of 0.5-10 μm. It is particularly advantageous to let such particles have a mean particle size, which is considerably smaller than the mean grain size of the binding agent, because then a somewhat higher initial filling density can be obtained. The amount of aggregate material is preferably 3-25 percent by weight of the finished CBC-material or 4-30 percent by volume of the mixture of the binding agent powder and the aggregate material prior to sludging the powder mixture.

In a special embodiment of the invention a fine-grained binding agent phase and a somewhat coarser aggregate material phase in the powder body are used instead. According to this embodiment the main portion of the powder grains in the binding agent phase can have grain sizes of 1-20 μm, while the main portion of the grains of the aggregate material phase have a size distribution of 5-50 μm. This choice of particle size distribution between the binding agent phase and the aggregate material phase will facilitate an almost total transformation or "consumption" of the binding agent, i.e. a reaction between the binding agent phase and the liquid. Consequently, the final CBC-product will be composed of comparatively large aggregate material particles, surrounded by completely hydrated areas and areas reacted in a corresponding way, respectively.

Further characteristic features and aspects of the invention are apparent from the claims and the following

description of some conceivable embodiments of a tool intended to be used in the carrying out of the method of the invention.

BRIEF DESCRIPTION OF DRAWINGS

In the following, reference will be made to some conceivable embodiments of a tool intended to be used for the carrying out ot the method, wherein reference will be made to the accompanying drawings, in which

Fig. 1 illustrates a first embodiment of the tool, a so called stopper to be used for the compaction and final dewatering of tooth fillings;

Fig. 2 shows the encircled tool head at a larger scale and in section;

Fig. 3 schematically at a still larger scale shows a surface portion of the active part of the stopper for the compaction and final dewatering, which part is encircled in Fig. 2; and

Fig. 4 shows another embodiment of the tool head.

DESCRIPTION OF SOME POSSIBLE EMBODIMENTS

The tool shown in Fig. 1 has an over all design which can be identical to that of conventional stoppers for making tooth fillings. The tool has a head 1, a neck 2 and a holder 3. The holder 3, the neck 2 and a shoulder 4 conventionally consists of steel. The characteristic feature of the tool is the tip portion 5 which consists of a porous but hard material. As above mentioned it can consist of a porous ceramic, a porous metallic, or a porous polymeric material. Also combinations of some of these materials are possible. Whatever material that it used, it shall exhibit continous pores having a size (diameter, i.e. size in the cross direction) which is so small that liquid can be sucked into the material through an efficient capillary action. Further the pores should be smaller than the grains in the pulverulent material to be compacted and dewatered by means of the stopper so that grains will not enter into and block the pores in the material in the tip portion 5. Thus it is recommended that the pores have a diameter not exceeding 50 μm, preferably not exceeding 30 μm, and that the majority of pores have a diameter smaller than 10 μm, preferably smaller than 1 μm. A ceramic material consisting of a so called reaction bounded silicon nitride is recommended as a tip portion material.

According to the embodiment shown in Fig. 2, the tip portion 5 consists of a detachable and exchangeable cylindrical member which can be secured in a recess 7 in the neck portion 4 by means of a male portion 6.

Fig. 4 illustrates another embodiment in which the interchangeable porous member 5' is not cylindrical but instead substantially conical. It is in this case secured to the neck portion 2' by means of a pin 7' on neck portion 2' and a corresponding recess 6' in the tip member 5'.

The detachable member 5 and 5', respectively, can when it has been saturated with liquid from the mass which is being compacted, be regenerated by heating in an oven or by a burner. The geometrical design naturally can be varied within wide ranges. The shown embodiments thus only are examples and do not limit the claimed patent protection.

Claims

1. Method for the manufacturing of a chemically bounded ceramic by reaction between one or several pulverulent binding agents and a liquid which reacts with these binding agents, wherein the ceramic product also can include one or several aggregates, which essentially do not take part in the chemical reactions, **characterized** in that a quantity of pulverulent material consisting of said one or several pulverulent binding agents and possibly said one or several aggregate material are blunged in said liquid, so that all grains of the powder are effectively brought to contact the liquid, that this slurry or slip thereafter is drained so that the main part of surplus reacting liquid is removed, that an amount of the mixture of powder and reacting liquid still existing to some extent in the mixture, i.e. to an extent larger than is required for the transformation of all pulverulent binding agent through chemical reaction, is applied in a mould cavity, and that additional liquid is removed in situ in the mould cavity before the product is hardened through reaction between the said binding agent and the remaining liquid.

2. Method according to claim 1, **characterized** in that said additional liquid is removed in situ by means of a compaction tool with a part acting on the moist pulverulent material, said part consisting of a hard, porous material, into which said additional liquid is sucked in at the same time as the pulverulent material is compacted in the mould cavity.

3. Method according to claim 1 or 2, **characterized** in that said slurry or slip after preconcentration is further concentrated in terms of its content of solid material to more than 55 volume-%, preferably to more than 60 volume-% and suitably to between 62 and 67 volume-%.

4. Method according to any of claims 1-3, **characterized** in that the preconcentration is carried out through centrifuging and/or dewatering in/or on a porous mould.

5. Method according to any of claims 1-4, **characterized** in that a compaction tool is used in which the pores in said porous material has a mean pore size which is smaller than the mean grain size of the powder mixture.

6. Tool for the compaction and for the removing of liquid from a moist, pulverulent tooth filling material in situ in a tooth cavity, **characterized** in that the part (5) of the tool working on the tooth filling material consists of a solid porous material.

7. Tool according to the claim 6, **characterized** in that the working part consists of a porous ceramic material.

8. Tool according to claim 6, **characterized** in that the working part consists of a porous metallic material.

9. Tool according to claim 6, **characterized** in that the working part consists of a porous polymeric material.

10. Tool according to any of claims 6-9, **characterized** in that the pores in the porous material have a mean pore diameter which is smaller than the mean grain size of the tooth filling material.

11. Tool according to any of claims 6-10, **characterized** in that the porous part is exchangeable.

12. Exchangeable member of a tool for the compaction and for the removing of liquid from a moist pulverulent tooth filling material in situ in a tooth cavity **characterized** in that it consists of a solid, porous material.

13. Exchangeable member according to claim 12, **characterized** in that it consists of a porous ceramic material.

14. Exchangeable member according to claim 12, **characterized** in that it consists of a porous metallic material.

15. Exchangeable member according to claim 12, **characterized** in that it consists of a porous polymeric material.

16. Exchangeable member according to any of claims 12-15, **characterized** in that the pores in the porous material have a diameter not exceeding 50 µm, preferably not exceeding 30 µm, and that the majority of the pores have a diameter smaller than 10 µm, preferably smaller than 1 µm.